

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



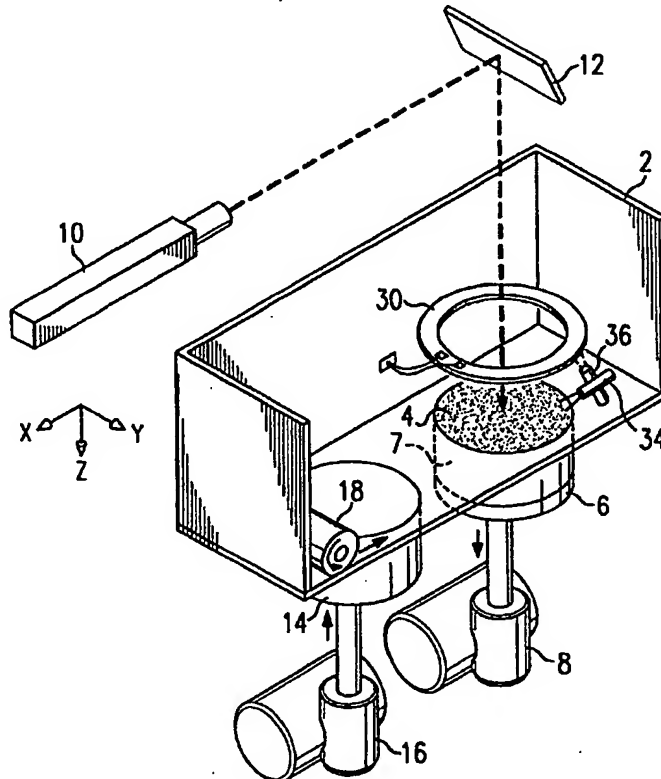
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B22F 3/105, 1/00		A1	(11) International Publication Number: WO 95/30503
			(43) International Publication Date: 16 November 1995 (16.11.95)
(21) International Application Number: PCT/US95/05579		(81) Designated States: CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
(22) International Filing Date: 5 May 1995 (05.05.95)		Published With international search report.	
(30) Priority Data: 08/239,205 6 May 1994 (06.05.94) US			
(71) Applicant: DTM CORPORATION [US/US]; Building 2, 1611 Headway Circle, Austin, TX 78754 (US).			
(72) Inventors: McALEA, Kevin, P.; 1204 Baylor Street, Austin, TX 78703 (US). BOOTH, Richard; 304 Camille Court, Pflugerville, TX 78660 (US). LAKSHMINARAYAN, Uday; 4210 Red River #305, Austin, TX 78751 (US). GIROUARD, Dan; 4903 Pony Chase Street, Austin, TX 78727 (US).			
(74) Agents: ANDERSON, Rodney, M. et al.; Vinson & Elkins L.L.P., 2500 First City Tower, 1001 Fannin Street, Houston, TX 77002-6760 (US).			

(54) Title: BINDER COMPOSITIONS FOR SELECTIVE LASER SINTERING PROCESSES

(57) Abstract

The composition and use of polymeric binders in fabricating parts by selective laser sintering. The binders are amorphous copolymers of methacrylic acid derivatives and may contain styrene and its derivatives, as well as additives, such as film forming agents and adhesion promoters. The binders are used to coat inorganic particulate substrates to create a powder comprised of the substrate and binder. The binders flow to form an interconnecting polymeric matrix upon the application of sufficient energy from the laser beam in a selective laser sintering process. Parts are thus fabricated by directing laser energy onto layers of the powder applied at a target surface (4) in successive fashion to build up a three-dimensional part comprised of a plurality of such layers. The part may then be subjected to a high temperature annealing process in a reducing environment, whereby the binders are virtually completely removed by thermal depolymerization of the copolymer, leaving an insignificantly small amount of residual ash.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

BINDER COMPOSITIONS FOR SELECTIVE LASER
SINTERING PROCESSES

FIELD OF THE INVENTION

This invention relates to the composition and use of polymer binders which permit the use of existing selective laser sintering technology for preparing prototype or "green" parts from CAD data bases by selective laser fusion at low temperatures of binder-coated inorganic particles. These binders are designed to impart the highest possible strength to the green parts produced by selective laser sintering at the lowest level of binder content. These binders are designed to be subsequently completely removed by thermal decomposition in either oxidizing or reducing environments to produce sintered parts that contain only metal, only ceramic, or only metal/ceramic materials. Alternatively, the binders can be left in place for some applications where lower functional temperatures and lower mechanical performance are permitted.

BACKGROUND OF THE INVENTION

A significant portion of the product design cycle of many modern manufactured products has generally been consumed by the time required to build and test prototype parts. Accordingly, many manufacturers operate fast turn-around shops for the production of prototype parts useful in the development of the manufactured product. One popular method of producing prototype parts in such shops is the subtractive machining of a block of material until the part matches the dimensions in a mechanical design. As is well known, the accuracy with which the machine prototype part matches the design can vary widely, primarily according to the skill of the machinist. In addition, the ability of subtractive processing to produce parts of complex shape is limited, and the time required for the machining of the part can be quite lengthy. As such, the product design cycle that depends upon subtractive machining of prototypes is often lengthy, delaying the time-to-market of the eventual manufactured product.

Accordingly, new methods for the producing of parts, especially prototypes, have been developed in recent years to enable the rapid manufacture of complex parts directly from computer-aided-design (CAD) databases. In particular, additive processes for building up the parts from a material have recently become popular, such processes in contrast to subtractive processes which remove material from a block to form the part.

A particularly successful and recently developed additive process is commonly referred to as selective laser sintering. According to the selective laser sintering process, a laser is scanned in raster fashion over a layer of fusible powder to fuse selected portions

of the layer according to a cross-section of the desired part. After the fusing of the desired portions of a layer, another layer of powder is placed and similarly selectively fused, with fused portions of the later layer fusing to fused portions of the previous layer.

Continued layer-wise processing in this manner results in a part which can be quite complex in the three-dimensional sense. This method is described in detail in U.S. Patent No. 5,076,869, issued December 31, 1991, and U.S. Patent No. 4,944,817, issued July 30, 1990, both assigned to the Board of Regents, the University of Texas System, and incorporated herein by this reference. The selective laser sintering method is also described in U.S. Patent No. 4,863,538, issued September 5, 1989, U.S. Patent No. 5,017,753, issued May 21, 1991, and U.S. Patent No. 4,938,816, issued July 3, 1990, all also assigned to Board of Regents, The University of Texas System, and incorporated herein by this reference.

By way of further background, U.S. Patent No. 5,156,697, issued on October 20, 1992, and U.S. Patent No. 5,147,587, issued on September 15, 1992, both also assigned to Board of Regents, The University of Texas System, and incorporated herein by this reference, as well as the other referenced U.S. Patents noted hereinabove, each describe the selective laser sintering of various materials and combinations of materials, such as plastics, waxes, metals, ceramics, and the like. In particular, the selective laser sintering method has been especially beneficial in the production of molds or cores useful in investment casting. For example, a part formed of a low-temperature wax by the selective laser sintering process may be used in the well-known "lost wax" method of forming an investment casting mold. In addition, the above-referenced U.S. Patent No. 5,156,697, issued on October 20, 1992, U.S. Patent No. 5,147,587, issued on

September 15, 1992, and U.S. Patent No. 5,182,170, issued on January 26, 1993, each describes methods for producing parts from high temperature materials, and thus may be useful in directly forming an investment casting mold.

5

In the selective laser sintering process, sufficient energy must be directed to the powder so as to cause it to fuse into the desired part cross-section. For metallic and ceramic powders processed in this manner, the fusing mechanism is sintering, in which the surface tension of the irradiated powder overcomes its viscosity, such that the particles flow together and bond. For such higher temperature materials, either higher power lasers must be used, or the temperature of the chamber in which the selective laser sintering process is carried out must be raised to near the sintering temperature. Accordingly, the production of parts of high melting point materials, such as metals and ceramics, is significantly more difficult than such production of lower melting point materials. For waxes and polymers (including polymer-coated metallic and ceramic powders), the melting point can be sufficiently low so that a low power laser (e.g., 25 watt or less, CO₂ laser) can cause the material to flow and fuse. As such, the temperature at which sintering occurs is substantially the melting or softening point of the powder material. (It will be understood that "sintering" of polymers and polymer-coated inorganic substrates by the selective laser sintering process refers to the softening and melting of such materials to cause them to flow and fuse, as opposed to the process whereby metallic or ceramic particles "sinter", which occurs below the melting part of such material).

35

In addition, thermal gradient-related effects such as warpage and shrinkage must also be controlled in the

selective laser sintering process, particularly for high temperature materials. Warpage has been observed in parts where a bottom flat surface curls up at the edges to become a curved surface, concave up. It is believed that such warpage is due to the thermal shrinkage of the sintered layer from its temperature during sintering to its post-sintering temperature, and, in some cases, the reduction in volume of a layer as it passes through the phase change from liquid to solid. The reduction in volume of a newly sintered layer, whether by phase change or by a drop in temperature, causes the top of the part to contract. The bottom of the part is thermally insulated by its immersion in unsintered powder and in previously sintered layers that have already contracted; as a result, contraction of the top layer induces stress that can corrode the part. Furthermore, uneven cooling of the part during its layer-wise manufacture, for example, where top layers of the part cooled more quickly than bottom layers, has also been observed to cause warpage and curling.

Also as noted hereinabove, some materials tend to shrink in the consolidation from powder to a high density solid that occurs in the sintering process. Particularly for high temperature materials, such shrinkage causes undesirable loss of dimensional accuracy.

Because of these thermal effects, it is therefore desirable to perform the selective laser sintering at relatively low temperatures, so that the thermal gradients present in the system are controlled. However, such low temperature processing is not compatible with the desire to form high strength, high temperature parts, such as molds or cores for investment casting.

Therefore, another method for producing parts of high temperature materials, such as high temperature ceramics, ceramic composites, and metals has been developed, which utilizes a powder of polymer-coated high temperature material, such as described in the above-
5 referenced U.S. Patent Nos. 5,076,869 and 4,944,817. As described in these Patents, after the formation of a part by flowing the polymeric binder to bind particles of a high temperature material, the precursor or "green" part
10 may be subjected to a high temperature, post-process anneal, in which the polymer coating dissociates and the remaining particles of the high-temperature material sinter together and form the part.

15 The binders are typically initially applied to the substrate particles by spraying, such as described in U.S. Patent No. 5,284,695, issued on February 8, 1994 and assigned to the Board of Regents, University of Texas System and incorporated herein by reference, or by
20 coating the binder onto the particles in a fluidized bed using conventional means. Thus, the binders must be capable of uniform application in either a sprayer or fluidized bed to coat as much of the inorganic particulate as possible and adhere to the inorganic
25 particulate substrate. Uniform, complete application of binder to substrate can be accomplished by dissolving the polymer in a suitable liquid organic solvent to achieve a low concentration of polymer, depositing the solution on the surface of the inorganic particle, then evaporating
30 the solvent to deposit the polymer. However, the problems of solvent recovery cost and potential environmental harm associated with the use of organic solvents largely preclude such a process. These problems can be avoided by using water as the vehicle for carrying
35 the binder during the spray or fluidized bed coating process. Because water soluble polymers do not work well

in the spray or fluidized bed coating process, the need for a water vehicle requires that the binder be highly dispersible in water, or water-emulsifiable.

5 It is important that the green part exhibit sufficient physical and mechanical properties to retain the desired shape and dimensions during handling and processing. One of the advantages of making parts by selective laser sintering rather than by more traditional
10 machining processes is that selective laser sintering allows the fabrication of intricate or complex parts with fine features without the labor and time required by machining. Such advantage would be lost if, for example, the green part were easily damaged or eroded during
15 handling and processing. For example, unfused particles often must be removed from the green part prior to high-temperature sintering. The preferred method of removing such loose particles is simply to brush the particles from the green part. Thus, the green part must be able
20 to withstand such brushing without the deterioration of its features or dimensions.

 One way to increase green part strength would be simply to maximize the amount of polymer binder.
25 However, as the binder dissociates upon high temperature sintering, void spaces are left behind. High levels of polymer binders result in relatively larger amounts of void spaces upon high temperature sintering, which can result in unacceptable amounts of shrinkage in the
30 finished part. Another problem with incorporating high levels of polymeric binder into the green part is that a higher binder content requires longer annealing or sintering times to remove the binder, which obviously reduces efficiency and adds costs. Therefore, it is
35 desirable to optimize binder levels to achieve maximum

physical and mechanical properties in the green part with a minimum of binder.

5 Binder levels may be optimized for use in the
present invention by selecting binders with optimal
chemical, mechanical, and flow properties. The binders
must flow sufficiently to fuse and thus bind the
substrate particles at the relatively low temperatures
10 used to create the green part in the selective laser
sintering process. However, the polymeric binder coating
must be rigid and non-tacky at room temperature to
prevent blocking or premature fusing of the powder during
transportation and storage and to provide sufficient
strength to the green part. Therefore, the binders must
15 have glass transition temperatures or melting points
sufficiently high to facilitate transportation and
storage, and yet sufficiently low to work well in the
selective laser sintering process.

20 In addition, the binders must "burn out" during high
temperature sintering to yield parts having a low ash
content. Most organic polymeric binders can be oxidized
to carbon dioxide and water in the high temperature, air
containing furnaces that are normally used to "fire" or
25 sinter ceramics. Similarly, almost any polymeric binder
can be burned out in a furnace, provided the furnace is
operated under oxidizing conditions first, to oxidize the
polymer followed by reducing conditions to reduce the
metal oxides formed during the previous step. This
30 technique, or one similar to it, may be used when
removing polypropylene or polyethylene and wax binders
from green parts made by powder injection molding. The
problem with this approach, however, is that extra
furnace processing time is required to reduce the metal
35 oxides. Also, some metal powder parts can swell due to
oxide formation, which can lead to unexpected changes in

part dimensions. It is well known in the prior art that polymers that have a tertiary carbon atom alternately located in their backbones depolymerize when heated. Not all such polymers, however, have the requisite mechanical and flow properties for use as binders in the selective laser sintering process.

One polymer/substrate material system used in conventional ceramics processes contains water soluble polymer binders and slip aids to coat the ceramic powder prior to furnace treatment. The binder-coated powder is typically mechanically compressed to shape prior to the furnace treatment that removes the polymer binder and thermally consolidates the ceramic material. However, compression pretreatment of metal or ceramic powder is not used or desired in selective laser sintering processing. Also, water soluble polymers are generally unsuitable for either the spraying or fluidized bed method of application.

It is an object of this invention to provide polymeric binder materials that form a coating on and adhere well to inorganic substrates during the selective laser sintering process to create an acceptably strong green part.

It is a further object of this invention to provide such polymeric binder materials where the inorganic substrates are metal and ceramic powders.

It is a further object of this invention to provide such polymeric binder materials that thermally decompose primarily by thermal depolymerization to monomer in a reducing atmosphere to yield gaseous products with little residue deposited on the inorganic substrate.

Other objects and advantages of the invention will be apparent to those of ordinary skill in the art having reference to the following specification, together with the drawings.

SUMMARY OF THE INVENTION

5 This invention enhances the utility of existing selective laser sintering technology by the composition and use of copolymer compositions having chemical structures that are optimized for binding high temperature inorganic particles with the laser beam in the selective laser sintering process to form accurately shaped and acceptably strong green parts comprised of the polymer bound inorganic particulate. The binders are used to coat an inorganic particulate substrate, such as metal and/or ceramic particles. These binders soften and flow at relatively low temperatures (between about 30°C and 100°C), and can be thermally removed in post selective laser sintering heat treatment processes without significant residual ash to yield structures that contain only metal and/or ceramic materials. These binders thus impart strength to the green part produced by the low temperature selective laser sintering process, but may be completely removed by post selective laser sintering heat treatment without affecting the characteristics of the finished metal and/or ceramic part.

25 The method of part production of the present invention includes the steps of depositing a first portion of powder, which is comprised of an inorganic substrate and a polymeric binder having the desired chemical and mechanical properties, onto a target surface, scanning the aim of a directed energy beam (preferably a laser) over the target surface, and sintering a first layer of the first powder portion on the target surface. The first layer corresponds to a first cross-sectional region of the part. The powder is sintered by operating the directed energy source when the aim of the beam is within the boundaries defining the

first layers. The sintering process thus melts the binder so that, upon cooling, an interconnecting matrix is formed. A second portion of powder is deposited onto the first sintered layer and the aim of the laser beam
5 scanned over the first sintered layer. A second layer of the second powdered portion is sintered by operating the directed energy source when the aim of the beam is within the boundaries defining the second layer. Sintering of the second layer also joins the first and second layers
10 into a cohesive mass, adding to the interconnecting matrix. Successive portions of powder are deposited onto the previously sintered layers, each layer being sintered in turn. The green part formed by this process is removed from the selective laser sintering apparatus and
15 may be subjected to a high temperature operation, where the binder material is driven off virtually completely and the inorganic substrate sintered to form a finished part having substantially the same shape and dimensions as the green part.

20

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic representation of the sintering apparatus of the present invention;

5 FIG. 2 is a schematic representation of the laser and the laser control apparatus of the present invention;

FIG. 3 is a schematic showing a portion of the layered build up of a part produced in accordance with the present invention, and illustrating the raster scan
10 pattern of the laser beam in the target area;

FIG. 4 is a perspective view of an example part produced in accordance with the present invention;

FIG. 5 is a sectional view with parts broken away and in phantom, of the part illustrated in FIG. 4;

15 FIG. 6 is a sectional view taken along line 7-7 of FIG. 4;

FIG. 7 illustrates coated powder of the present invention;

20 FIG. 8 illustrates the interconnecting polymeric matrix surrounding inorganic substrate particles after selective laser sintering;

FIG. 9 illustrates any two inorganic substrate particles surrounded by the interconnecting polymeric matrix.

25

DETAILED DESCRIPTION OF THE INVENTION

An apparatus for performing selective laser sintering according to the present invention will now be described relative to the schematic representation illustrated in FIG. 1. The apparatus of FIG. 1 includes a chamber 2 (front doors and the top of chamber 2 are not shown in FIG. 1, for purposes of clarity), within which the selective sintering process takes place. Target surface 4, for purposes of the description herein, refers to the top surface of heat-fusible powder (including portions previously sintered, if present) disposed on part piston 6; the sintered and unsintered powder disposed on part piston 6 will be referred to herein as part bed 7. The vertical motion of part piston 6 is controlled by motor 8. Laser 10 provides a beam which is reflected by galvanometer-controlled mirrors 12 (only one of which is shown for clarity), in the manner described in the U.S. Patents referred to hereinabove and as shown in FIG. 2.

FIG. 2 illustrates laser 10 and the apparatus for its control. The components of the laser system are shown in FIG. 2 as integrated within laser head 10. Laser head 10 thus includes such conventional control elements as described in the above-referenced U.S. Patent No. 4,863,538, for example a safety shutter, a front mirror assembly, and focusing elements such as diverging and converging lenses. The type of laser 10 used is of course dependent upon many factors, and in particular upon the type of powder that is to be sintered. A preferred laser is a Synrad Model C48-115 CO₂ laser. Laser 10 is preferably controllable to be modulated on and off; while on, laser 10 produces laser beam 5 which travels generally along the path shown by the arrows in FIG. 2.

Computer 40 and scanning system 42 are also included for controlling the direction of the laser beam as it impinges target surface 4. In this preferred embodiment, scanning system 42 includes a microprocessor for
5 controlling laser 10, and computer 40 generates the data by which the dimensions of the part to be produced is defined. A conventional personal computer workstation, such as a model 486-33 manufactured and sold by Mobius Computer Corporation, based on an 80486DX-33
10 microprocessor as manufactured and sold by Intel Corporation, is suitable for use as computer 40 in the preferred embodiment. Computer 40 also controls the operation of the overall system, including control of the dispensing of powder and of the temperature and gas flow
15 conditions within chamber 2, in the manner described hereinbelow relative to the preferred embodiment of the invention.

Scanning system 42 includes prism 44 for redirecting
20 the path of travel of the laser beam; the number of prisms 44 necessary for directing the laser beam to the proper location is based on the physical layout of the apparatus. Alternatively, as is well known in the art, one or more fixed mirrors can be used in place of prism
25 44 for directing laser beam 5 from laser 10 to the scanning system 42, depending upon the particular layout of the equipment. Scanning system 42 further includes a pair of mirrors 46, 47 which are driven by respective galvanometers 48, 49. Galvanometers 48, 49 are coupled
30 to their respective mirrors 46, 47 to selectively orient the mirrors 46, 47 and control the aim of laser beam 5. Galvanometers 48, 49 are mounted perpendicularly to one another so that mirrors 46, 47 are mounted nominally at a right angle relative to one another. Scanning system 42
35 controls the movement of galvanometers 48 and 49 and thus the aim of laser beam 5 within target surface 4, in

conjunction with on and off modulation of the laser, which is controlled by computer 40. Scanning system 42 is coupled to computer 40 so that the CAD/CAM data within computer 40 can be realized in the directional control of the laser beam via mirrors 46, 47. It is contemplated that alternative scanning systems may be used in place of scanning system 42, including such apparatus as acousto-optic scanners, rotating polygonal mirrors, and resonant mirror scanners.

Referring back to FIG. 1, delivery of the heat-fusible powder is accomplished in the apparatus of FIG. 1 by way of powder piston 14, controlled by motor 16, and by counter-rotating roller 18. As described in above-referenced U.S. Patent No. 5,017,753, counter-rotating roller 18 transfers the powder lifted above the floor of chamber 2 to the target surface 4 in a uniform and level fashion. As described in U.S. Patent No. 5,252,264, issued October 12, 1993, assigned to DTM Corporation, and incorporated herein by this reference, it may be preferred to provide two powder pistons 14 on either side of part piston 6, for purposes of efficient and flexible powder delivery.

In operation, the apparatus of FIG. 1 supplies powder to chamber 2 via powder piston 14; powder is placed into chamber 2 by the upward partial motion of powder piston 14 provided by motor 16. Roller 18 (preferably provided with a scraper to prevent buildup, said scraper not shown in FIG. 1 for clarity) spreads the powder within the chamber by translation from powder piston 14 toward and across target surface 4 at the surface of part bed 7 above part piston 6, in the manner described in the above-referenced U.S. Patent No. 5,017,753 and U.S. Patent No. 5,252,264. At the time that roller 18 is providing powder from powder piston 14,

target surface 4 (whether a prior layer is disposed thereat or not) is preferably below the floor of chamber 2 by a small amount, for example 5 mils, to define the thickness of the powder layer to be processed. It is preferable, for smooth and thorough distribution of the powder, that the amount of powder provided by powder piston 14 be greater than that which can be accepted by part cylinder 6, so that some excess powder will result from the motion of roller 18 across target surface 4; this may be accomplished by the upward motion of powder piston 14 by a greater amount than the distance below the floor of chamber 2 that target surface 4 is set at (e.g., 10 mils versus 5 mils). It is also preferable to slave the counter-rotation of roller 18 to the translation of roller 18 within chamber 2, so that the ratio of rotational speed to translation speed is constant.

Further in operation, after the transfer of powder to target surface 4, and the return of roller 18 to its original position near powder piston 14, laser 10 selectively sinters portions of the powder at target surface 4 corresponding to the cross-section of the layer of the part to be produced, in the manner described in the above-referenced U.S. Patents and pending applications. A particularly beneficial method of controlling the thermal selective laser sintering mechanism by controlling the scanning of the laser beam is disclosed in copending application S.N. 07/992,926, filed December 18, 1992, assigned to DTM Corporation, and incorporated herein by this reference. After completion of the selective sintering for the particular layer of powder, part piston 6 moves downward by an amount corresponding to the thickness of the next layer, awaiting the deposition of the next layer of powder from roller 18 to be added to part bed 7.

Turning to FIG. 3 of the drawing, a portion of a green part 52 is schematically illustrated and shows four layers 54-57. The aim of the laser beam 5 in FIG. 3, is directed in a raster scan pattern as at 66. As used
5 herein, "aim" is used as a neutral term indicating direction, but does not imply the modulation state of the laser 10. For convenience, the axis 68 is considered the fast scan axis, while the axis 70 is referred to as the slow scan axis. Axis 72 is the direction of part build-
10 up.

Turning to FIG. 7, powders according to the present invention are illustrated. FIG. 7 illustrates powder particles 22 comprised of an inorganic substrate 91
15 coated with binder 90. Powder particles 22 may range in size from 10 to 300 microns. Inorganic substrate 91 can be metal, ceramic or a combination thereof. When metal is used as inorganic substrate 91, the type of metal used depends upon the specific application intended for the
20 finished part. For example, for tooling applications, low carbon steel, such as 1018 steel, is preferred, but higher carbon steel, such as 1080 steel may be used. Stainless steel or tool steel may also be used as inorganic substrate 91 for tooling applications, but
25 costs much more than low carbon steel and the alloy components of stainless steel can pose disposal problems. It will be appreciated that a wide variety of applications can be accommodated by the selective laser sintering process by using a wide variety of materials
30 for inorganic substrate 91. Aluminum and tungsten carbide are often used as inorganic substrate 91 for a variety of applications. Several ceramic systems may be used, including glass, alumina, silica-zircon, silicon nitride, and silicon carbide. Of course, those skilled
35 in the art will understand that other inorganic

substrates may be used, such as but not limited to iron, copper, and cobalt.

5 Still referring to FIG. 7, binder 90 is comprised of a thermoplastic polymeric material. Binder 90 is coated onto inorganic substrate 91 by conventional coating processes, such as by spraying or coating in a fluidized bed. Also, binder 90 is preferably substantially water insoluble, for ease of coating and so that its flow
10 characteristics are independent of relative humidity. The temperature to be obtained during the sintering process will cause binder 90 to flow but is insufficient to cause inorganic substrate 91 to flow.

15 Upon application of sufficient energy supplied by the laser, as described herein, binder 90 will flow and fuse to form an interconnecting polymeric matrix 100, as shown in FIG. 8. Polymeric matrix 100 functions to bind particles of inorganic substrate 91. In another
20 preferred embodiment of the present invention, the temperature of the powder mass may be increased using conventional heating means, allowing the laser beam to supply merely a small increase of energy to cause binder 90 to flow.

25 Referring now to FIG. 7, binder 90 must flow sufficiently at the relatively low temperatures used in the selective laser sintering process to form polymeric matrix 100 (FIG. 8). On the other hand, binder 90 must
30 be rigid and non-tacky at room temperature, so that premature fusing or blocking does not occur during transportation and storage of the powder, thus creating difficulties in handling. As a result, binder 90 has a glass transition temperature (for amorphous polymers) or
35 a melting point (for semicrystalline polymers) between 30°C and 100°C. Commercially available binders having a

melt flow index greater than 0.05 grams/10 minutes at 200°C and 75 psi extrusion pressure have sufficient flow characteristics (i.e., sufficiently low melt viscosities) to work in this invention at a binder content of less than 10% by volume in the green part. NeoCryl A-639, NeoCryl A-622, NeoCryl A-601 are examples of such commercially available binders from Zeneca Resins, 730 Main Street, Wilmington, Massachusetts 01887-3386. NeoCryl A-639 is an amorphous copolymer comprised of butyl methacrylate and styrene, and has a glass transition temperature of 62°C. NeoCryl A-622 is an amorphous copolymer comprised of butyl methacrylate and styrene, and has a glass transition temperature of 34°C. NeoCryl A-601 is an amorphous copolymer comprised of methyl methacrylate and butyl methacrylate, and has a glass transition temperature of 56°C. NeoCryl A-639, NeoCryl A-622 and NeoCryl A-601 also contain small amounts of film forming agents, flow agents, and adhesion promoters. NeoCryl A-622 and NeoCryl A-601 further contain plasticizers. These added ingredients, particularly the film forming agents, adhesion promoters and plasticizers, are thought to enhance the coating and flow properties of the binders.

Because these binders contain tertiary carbon atoms located alternately along their backbones, the binders decompose upon heating primarily by depolymerization to monomer. Thermogravimetric analysis indicates that these binders decompose almost completely, leaving less than 0.5% by weight residue of the binder coated on the inorganic particulate substrate. The decomposition products are typically gaseous and substantially non-toxic, except for styrene monomer produced upon the decomposition of styrene-containing copolymers and any toxic by-products that might inadvertently be produced during thermal decomposition.

FIG. 9a illustrates any two inorganic substrate particles 91 encased by polymeric matrix 100 after selective laser sintering. As is well known in the art, the failure mechanism of the structure illustrated in FIG. 9a depends, in part, on the adhesion characteristics of binder 90. If binder 90 sufficiently adheres to inorganic substrate particle 91, upon the application of sufficient stress to the structure illustrated in FIG. 9a, (for example, in the directions indicated in FIG. 9b) such a structure fails by cohesive failure within polymeric matrix 100 (as opposed to adhesive failure between polymeric matrix 100 and inorganic substrate particle 91), as shown in FIG. 9c. The binders of the present invention have been shown to fail by cohesive rather than by adhesive failure. Thus, the mechanical properties of green part 52 are largely dependent upon the mechanical properties of polymeric matrix 100, which in turn, depends on the mechanical properties of binder 90.

It is well known in the art that all polymer melt viscosities for a given polymer increase with the molecular weight of the polymer. Thus, lowering the molecular weight of a given polymer decreases its melt viscosity and consequently enhances its flow characteristics. However, it is also well known in the art that for a given polymer, mechanical properties decrease with decreasing molecular weight. The binders of the present invention optimize flow characteristics and mechanical properties, in part, by not sacrificing molecular weight to obtain acceptable flow characteristics. It is contemplated that commercially available binders of the present invention, having a weight average molecular weight of at least 100,000 and a melt flow index of greater than 0.05 grams/10 minutes measured at 200°C and 75 psi extrusion pressure, will

allow the production of acceptably strong green parts by the selective laser sintering process. For example, NeoCryl A-639 has a melt flow index of 0.73 grams/10 minutes at 200°C and 75 psi extrusion pressure and a weight average molecular weight of about 500,000. NeoCryl A-601 has a melt flow index of 0.21 grams/10 minutes at 200°C and 75 psi extrusion pressure and a weight average molecular weight of 509,000. NeoCryl A-622 has a melt flow index of 116 grams/10 minutes at 200°C and 75 psi extrusion pressure and a weight average molecular weight of 429,000.

The relatively high molecular weights of these binders allow the production of acceptably strong green parts at lower binder levels than would be possible for lower molecular weight materials. For example, when NeoCryl A-639, NeoCryl A-601 or A-602 is used as binder 90, green part 52, illustrated in FIG. 4, exhibits strengths at failure of 300-500 psi at a binder content of less than 10% by volume, as measured in a three-point bending test.

The fluidized bed coating process typically produces uniformly coated particles, as depicted schematically in FIG. 7. The spray drying process, on the other hand, tends to produce incompletely coated, agglomerated particles, with some amount of exposed substrate surface, as described in above-referenced U.S. Patent No. 5,284,695. Thus, it is believed that binders applied by the spray drying process require enhanced melt flow properties relative to binders applied by the fluidized bed process, because the spray dried binders must flow over more surface area of the substrate particles to fuse sufficiently at the relatively low temperatures used in the selective laser sintering process. The fluidized bed coating process or any other process that produces well

coated particles therefore allows the use of materials having a broader range of melt flow indices relative to the spray drying process, and is preferred. NeoCryl A-639, NeoCryl A-622, and NeoCryl A-601 all have been shown to allow the fabrication of acceptably strong green parts by selective laser sintering when coated upon substrate particles by the fluidized bed process. Because NeoCryl A-622 and NeoCryl A-601 contain plasticizers, it is believed that both NeoCryl A-622 and A-601 could be applied to the substrate particles by the spray drying process with acceptable results. Thus, even at relatively high molecular weights, the binders of the present invention may be applied to the substrate by a variety of means, and flow sufficiently at the relatively low temperatures used in the selective laser sintering process.

In FIGS. 4 and 5, an example green part 52 is illustrated. As can be seen from the drawing, the example green part 52 assumes an unusual shape in that it is not symmetrical and would be difficult to fabricate using conventional machining methods. For reference purposes, the green part 52 includes an outer base structure 80 having an interior cavity 82 and a pillar 84 disposed within the cavity 82 (see FIG. 4). As shown in FIG. 5, some of the powder 22 is loose, while the remainder of the powder is selectively sintered to comprise the structure of the green part 52. FIG. 5 is shown in vertical section with parts broken away and outlined in phantom to show the sintered cohesive portions of the green part 52.

FIG. 6 shows a horizontal cross-sectional region, taken along line 7-7 of FIG. 4. FIG. 6 represents a discrete layer 86 associated with the cross-sectional region of the part being produced. As such, the sintered

layer 86 of FIG. 6 is a product of a single raster pattern 66 as illustrated in FIG. 3.

As can be seen from the example illustrated in FIG. 4, parts of complex shape can be produced with relative ease. Those skilled in the art will appreciate that the green part 52 illustrated in FIG. 4 would be difficult to produce using conventional machining methods. In particular, machine tool access would make the fabrication of cavity 82 and pillar 84 difficult, if not impossible, to produce if the green part 52 were of a relatively small size.

In addition to avoiding the access problem, it will be appreciated that the production accuracy is not dependent upon machine tool wear and the accuracy of mechanical components found in conventional machine tools. That is, the accuracy and tolerances of the parts produced by the method and apparatus of the present invention are primarily a function of the quality of the electronics, the optics, and the implementing software. Of course, heat transfer and material considerations do affect the tolerances obtainable.

Those skilled in the art will appreciate that conventional machining techniques require considerable human intervention and judgment. For example, a conventional machining process, such as milling, would require creativity to make such decisions as tool selection, part segmenting, sequence of cuts, etc. Such decisions would even be more important when producing a control tape for a tape control milling machine. On the other hand, the apparatus of the present invention only requires the data relating to each cross-sectional region of the part being produced. While such data can be simply programmed into the computer 40, preferably, the

computer 40 includes a CAD/CAM system. That is, the CAD/CAM portion of the computer 40 is given the overall dimensions and configurations of the desired part to be produced and the computer 40 determines the boundaries for each discrete cross-sectional region of the part. Thus, a vast inventory of part information can be stored and fed to the computer 40 on a selectable basis. The apparatus illustrated in FIG. 1 produces a selected part without set-up time, part specific tooling, or human intervention. Even the complex and expensive dies associated with powder metallurgy and conventional casting techniques are avoided.

While large quantity production runs and certain part material characteristics might be most advantageously made using conventional fabrication techniques, the method and apparatus of the present invention is useful in many contexts. In particular, prototype models and casting patterns are easily and inexpensively produced. For example, casting patterns are easily made for use in sand casting, lost wax casting, or other forming techniques. Further, where desired quantities are very small, such as with obsolete replacement parts, production of such replacement parts using the apparatus of the present invention has many advantages. Finally, the use of the apparatus may be useful where size of production facilities is a major constraint, such as on-ship or in outerspace.

Post-sintering heat treatment of green part 52 (FIG. 4) is preferably carried out in a conventional microprocessor-controlled furnace (not shown) in two steps. In the first step, the furnace is ramped to 200-400°C at a rate of 1-5°C/minute and held at that temperature for 1-10 hours, depending on the size of green part 52, in a reducing atmosphere, to remove the

binder. As the size of green part 52 increases, more time and a higher temperature are required to burn out the binder. Hydrogen is continually added to the furnace to provide the reducing atmosphere. The furnace is then
5 ramped to approximately 1000°C at a rate of 1-5°C/minute and held at 1000°C for 1-10 hours, again depending upon the size of green part 52, and then cooled to room temperature. After cooling, a relatively low temperature melting material, such as copper or bronze, is added to
10 the part. The addition of this relatively low temperature melting material helps reduce shrinkage in the finished part by filling the volume created by the dissociation of binder 90. In this step, the relatively low temperature melting material is placed in contact
15 with the part, and the temperature of the furnace is then increased to a temperature above the sintering temperature of the high temperature material, typically 1080-1100°C, and the low temperature melting material is allowed to infiltrate the part, and the inorganic
20 substrate particles are fused. The resultant finished part is typically comprised of about 50% of the high melting temperature material that originally comprised green part 52 and about 50% of the low melting temperature material added during post-sintering heat
25 treatment. Parts made in this fashion using the binders described herein exhibit less than 2% linear dimensional shrinkage in all three axes.

Alternatively, the post-sintering heat treatment may
30 also be carried out in a single step or not at all. The green part 52 formed by the selective laser sintering process, using the binders of the present invention, may have sufficient structural integrity to serve as the prototype part, in which case the post-sintering heat
35 treatment is not performed.

While the invention has been described herein
relative to its preferred embodiments, it is of course
contemplated that modifications of, and alternatives to
these embodiments, such modifications and alternatives
5 obtaining the advantages and benefits of this invention,
will be apparent to those of ordinary skill in the art
having reference to this specification and its drawings.
It is contemplated that such modifications and
alternatives are within the scope of this invention as
10 subsequently claimed herein.

WHAT IS CLAIMED IS:

1. A powder for use in a selective laser sintering process, comprising a substrate coated with a polymeric binder, wherein said binder is comprised of an amorphous copolymer having a melt flow index of greater than 0.05 grams/10 minutes at 200°C and 75 psi extrusion pressure and a weight average molecular weight of at least 100,000.
2. The powder of claim 1, wherein said binder thermally decomposes upon heating in a reducing environment to yield gaseous products and a residue deposited on said substrate of less than 0.5% by weight of the binder coated on said substrate.
3. The powder of claim 1, wherein said copolymer has a glass transition temperature between 30°C and 100°C.
4. The powder of claim 1, wherein said substrate comprises a metal.
5. The powder of claim 1, wherein said substrate comprises a ceramic.
6. The powder of claim 1, wherein said substrate comprises a combination of a metal and a ceramic.
7. The powder of claim 3, wherein said copolymer comprises butyl methacrylate and styrene.
8. The powder of claim 3, wherein said copolymer comprises methyl methacrylate and butyl methacrylate.

9. The powder of claim 1, wherein said binder further comprises a film forming agent and an adhesion promoter.

5 10. The powder of claim 9, wherein said binder further comprises a plasticizer.

11. The powder of claim 1, wherein said binder is substantially insoluble in water.

10 12. The powder of claim 1, wherein said powder ranges in size from 10 to 300 microns.

13. The powder of claim 2, wherein said binder thermally decomposes upon heating in a reducing environment primarily by depolymerization to monomer.

14. A method for producing a part, comprising the steps of

20 (a) applying a layer of a powder comprised of a substrate coated with a binder comprised of an amorphous copolymer having a melt flow index of greater than 0.05 grams/10 minutes at 200°C and 75 psi extrusion pressure and a weight average molecular weight of at

25 least 100,000 at a target surface;

 (b) directing energy at selected locations of said layer corresponding to a part cross-section to fuse said binder to form an interconnecting polymeric matrix;

 (c) repeating said applying and directing

30 steps to form a three-dimensional part in layerwise fashion; and

 (d) removing unfused powder from said part.

15. The method of claim 14, wherein said binder thermally decomposes upon heating in a reducing environment to yield gaseous products and a residue

deposited on said substrate of less than 0.5% by weight of the binder coated on said substrate.

5 16. The method of claim 14, wherein said copolymer comprises an amorphous copolymer having a glass transition temperature between 30°C and 100°C.

10 17. The method of claim 14, wherein said substrate comprises a metal.

18. The method of claim 14, wherein said substrate comprises a ceramic.

15 19. The method of claim 14, wherein said substrate comprises a combination of a metal and a ceramic.

20 20. The method of claim 16, wherein said copolymer comprises butyl methacrylate and styrene.

21. The method of claim 16, wherein said copolymer comprises methyl methacrylate and butyl methacrylate.

25 22. The method of claim 14, wherein said binder further comprises a film forming agent and an adhesion promoter.

23. The method of claim 22, wherein said binder further comprises a plasticizer.

30 24. The method of claim 14, wherein said binder is substantially insoluble in water.

35 25. The method of claim 14, wherein said powder ranges in size from 10 to 300 microns.

26. The method of claim 14, wherein said binder comprises less than 10% by volume of said part.

5 27. The method of claim 15, wherein said binder thermally decomposes upon heating in a reducing environment primarily by depolymerization to monomer.

28. The method of claim 14, further comprising the step of heating said part in a reducing environment to a
10 temperature sufficient to remove said binder;

29. The method of claim 28, further comprising the steps of

15 (a) adding a filler material to said part;
(b) forming a finished part by heating said part and filler material to above the melting point of said filler material and above the fusing temperature of said substrate.

20 30. The method of claim 29, wherein said filler material is selected from the group consisting of copper and bronze.

25 31. A part produced by the method comprising the steps of:

30 (a) applying a layer of a powder comprised of a substrate coated with a binder comprised of an amorphous copolymer having a melt flow index of greater than 0.05 grams/10 minutes at 200°C and 75 psi extrusion pressure and a weight average molecular weight of at least 100,000 at a target surface;

(b) directing energy at selected locations of said layer corresponding to a part cross-section to fuse said binder to form an interconnecting polymeric matrix;

(c) repeating said applying and directing steps to form a three-dimensional part in layerwise fashion; and

(d) removing unfused powder from said part.

5

32. The part of claim 31, wherein said binder thermally decomposes in a reducing environment to yield gaseous products and a residue deposited on said substrate of less than 0.5% by weight of the binder coated on said substrate.

10

33. The part of claim 31, wherein said copolymer comprises an amorphous copolymer having a glass transition temperature between 30°C and 100°C.

15

34. The part of claim 31, wherein said substrate comprises a metal.

35. The part of claim 31, wherein said substrate comprises a ceramic.

20

36. The part of claim 31, wherein said substrate comprises a combination of a metal and a ceramic.

25

37. The part of claim 33, wherein said copolymer comprises butyl methacrylate and styrene.

38. The part of claim 33, wherein said copolymer comprises methyl methacrylate and butyl methacrylate.

30

39. The part of claim 31, wherein said binder further comprises a film forming agent and an adhesion promoter.

35

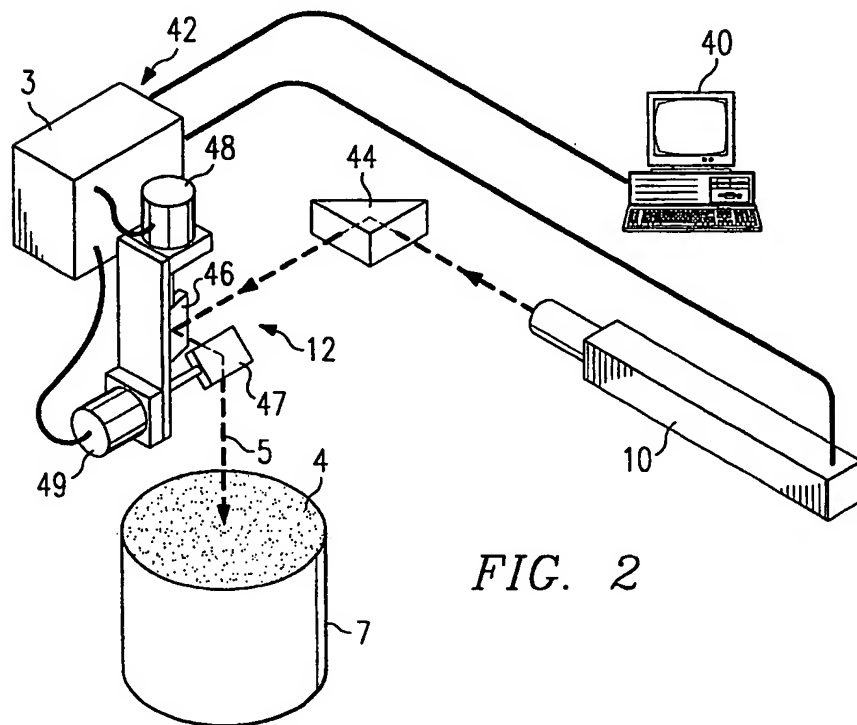
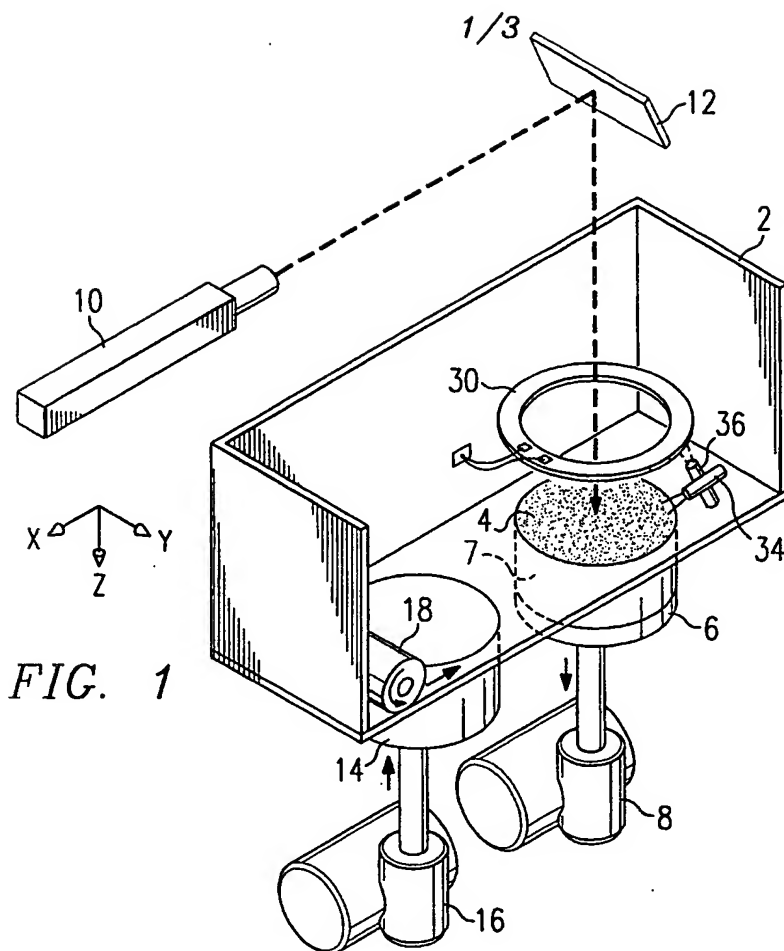
40. The part of claim 39, wherein said binder further comprises a plasticizer.

41. The part of claim 31, wherein said binder is substantially insoluble in water.

5 42. The part of claim 31, wherein said powder ranges in size from 10 to 300 microns.

43. The part of claim 31, wherein said binder comprises less than 10% by volume of said part.

10 44. The part of claim 32, wherein said binder thermally decomposes upon heating in a reducing environment primarily by depolymerization to monomer.



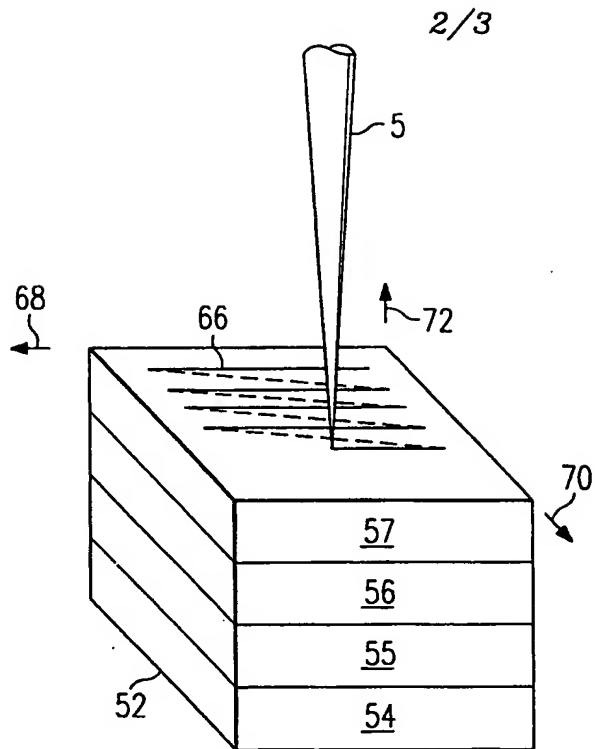
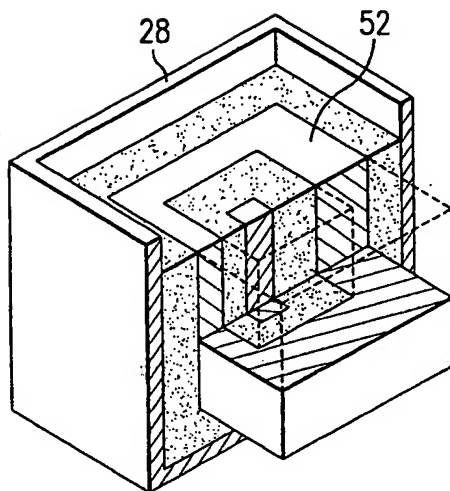
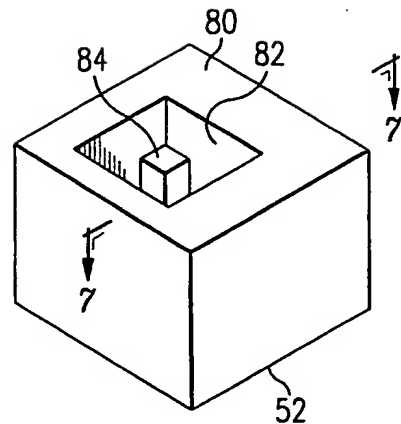


FIG. 4



3/3

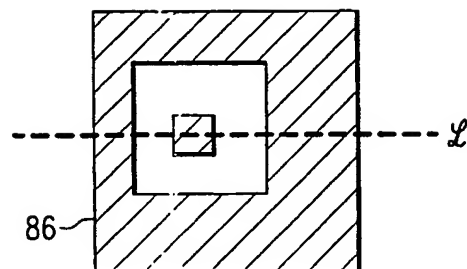


FIG. 6

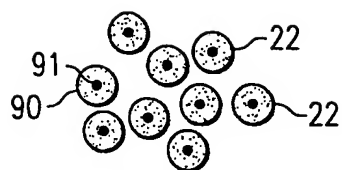


FIG. 7

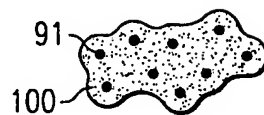


FIG. 8



FIG. 9A

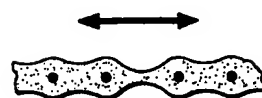


FIG. 9B



FIG. 9C

0

INTERNATIONAL SEARCH REPORT

 Internat Application No
 PCT/US 95/05579

 A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 B22F3/105 B22F1/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B22F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO-A-93 22469 (HOEGANAES CORP) 11 November 1993 see claims 1,9,16-18,21,22; example 1 ---	1-44
Y	US-A-5 284 695 (BARLOW JOEL W ET AL) 8 February 1994 cited in the application see column 4, line 59 - column 5, line 6; claims 1-3,8,14-18 ---	1-44
A	WO-A-85 00305 (INLAND STEEL CO) 31 January 1985 see page 38, line 4 - line 23 -----	3

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- * "A" document defining the general state of the art which is not considered to be of particular relevance
- * "E" earlier document but published on or after the international filing date
- * "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- * "O" document referring to an oral disclosure, use, exhibition or other means
- * "P" document published prior to the international filing date but later than the priority date claimed

- * "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- * "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- * "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- * "&" document member of the same patent family

Date of the actual completion of the international search

11 August 1995

Date of mailing of the international search report

25. 08. 95

Name and mailing address of the ISA

 European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
 Fax: (+ 31-70) 340-3016

Authorized officer

Schruers, H

D

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat Application No

PCT/US 95/05579

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9322469	11-11-93	US-A- 5290336	01-03-94
		EP-A- 0639232	22-02-95
		JP-T- 7505924	29-06-95

US-A-5284695	08-02-94	US-A- 4944817	31-07-90
		US-A- 5076869	31-12-91
		AU-B- 3922393	21-10-93
		WO-A- 9319019	30-09-93
		AU-B- 643700	25-11-93
		AU-A- 6206590	14-03-91
		CA-A- 2024592	06-03-91
		EP-A- 0416852	13-03-91
		JP-A- 3183530	09-08-91
		US-A- 5431967	11-07-95
		US-A- 5382308	17-01-95
		US-A- 5156697	20-10-92
		US-A- 5147587	15-09-92
		US-A- 5182170	26-01-93
		US-A- 5296062	22-03-94

WO-A-8500305	31-01-85	US-A- 4542048	17-09-85
		CA-A- 1238825	05-07-88
		EP-A- 0148938	24-07-85
		US-A- 4628004	09-12-86
		US-A- 4678717	07-07-87
